II. MICROWAVE SPECTROSCOPY*

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A. SECOND-HARMONIC SPECTROSCOPY

A preliminary experiment has been done to evaluate empirically the sensitivity of a second-harmonic EPR spectrometer. A sample of diphenylpicrylhydrazyl (DPPH) was excited by a 1-kW pulse of 14.35 GHz radiation of 0.75 μs duration in the field of the rectangular TE_{011} mode of the cavity. The second-harmonic radiation emitted by the DPPH sample into the rectangular TE_{022} mode was detected with a superheterodyne receiver at 28.70 GHz. The sample of 10^{19} free radicals had a resonance linewidth of a few Gauss.

When the source second harmonic was suppressed to a level below receiver noise by a filter of 10 shunt cavities resonant at 28.70 GHz and the Zeeman frequency was adjusted to equal twice the driving microwave frequency, the second harmonic coming from this sample and detected by the receiver was 70 dB above receiver noise.

This indicates that this system has a sensitivity of 10^{12} spins/G linewidth-square root filter time constant. The best conventional EPR spectrometers have a sensitivity that is ten times greater, but for an initial experiment the sensitivity of the second-harmonic EPR spectrometer is very promising.

Work is in progress to evaluate empirically the sensitivity of a second-harmonic gas microwave spectrometer. The second-harmonic Stark spectrum of the ammonia rotation-inversion spectrum will be measured. A Stark cavity appropriate for this experiment has been designed and tested for its microwave properties. In operation the 3-3 ammonia resonance will be tuned through the cavity resonance with the applied Stark field.

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